FLUID INCLUSION AND STABLE ISOTOPE CONSTRAINTS ON TEMPERATURE AND PRESSURE OF VEIN FORMATION; HUDSON VALLEY FOLD-THRUST BELT, CATSKILL, N.Y.

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ABSTRACT: Syntectonic veins in the Hudson Valley Fold-Thrust Belt near Catskill, New York contain vugs that host well-formed calcite and quartz crystals. Stable isotope analyses of co-existing calcite and quartz suggest that the temperature of vein mineralization was between 219 and 315°C at three sampling localities. Fluid inclusions in quartz crystals from syntectonic veins consist of two-phase water+methane and form alternating primary inclusion bands. Homogenization temperatures of water + methane inclusions record mineral precipitation in the range 236-291°C. Burial depth during vein formation was in the range 3.2-4.8 kilometers based on isochore intersection determination of pressure and assumption of near hydrostatic pressures during vein formation. Assuming lithostatic pressure, burial depths were in the range 1.4-2.1 km. Melting temperatures of water ice indicate fluid salinity near seawater. Calculation of the isotopic composition of waters in equilibrium with syntectonic vein minerals and with host limestone and chert suggest that mineralizing fluids had equilibrated with the host strata. The relatively high geothermal gradient (>40°C per km) required suggests derivation of fluids from a more deeply buried portion of the foreland basin to the west, or local heating of fluids by igneous rocks that intruded at depth beneath the study area.

INTRODUCTION

The Hudson Valley Fold-Thrust Belt (HVB of Marshak 1986) is a narrow zone of deformed Silurian and Devonian rock that borders the Hudson River between Albany and Kingston, New York. It is bounded on the east by the Taconic Mountains and on the west by flat-lying Devonian clastic sedimentary rocks of the Catskill Platteau. Structures within the HVB are similar to those found in the Valley and Ridge Province of the Appalachians to the southwest, but fold axes within the HVB are mainly oriented north-south. Change in structural orientation near Kingston, New York suggests that the HVB is not simply an extension of the Valley and Ridge Province (Marshak 1986). Fold-thrust structures within the HVB are best defined within Silurian and Devonian strata, although older rocks within the Taconic Range were involved in HVB deformation (Ratcliffe and Harwood 1975).

The youngest deformed rocks in the HVB are middle Devonian Onondaga Formation, but the age relationship of HVB deformation to other late Paleozoic tectonic episodes within the Appalachians is not clear. Marsak (1986b) linked HVB deformation to the Medial-Late Devonian Acadian event (c. 370 mya) rather than the Pennsylvanian-Permian Alleghenian Orogeny (c. 280 mya), since Upper Devonian strata west of the HVB are not structurally deformed. Fission-track and vitrinite reflectance data (Gurney and Friedman 1986) suggest that Devonian rocks west of the HVB reached temperatures that might indicate burial depths of 7-8 kilometers. In addition, fluid inclusion and stable isotope data indicate temperatures in the range 140-210°C during precipitation of diagenetic mineral phases in Paleozoic rocks in central New York State (Friedman 1987a, 1987b; Golam and Friedman 1995). These authors have argued for burial depths that require deposition of 4-7 km of post-Devonian strata in the present Catskill Mountain region. Such burial depths must have occurred well after the Acadian to allow for accumulation of a thick late Paleozoic sediment pile, and if HVB deformation took place at elevated pressures and temperatures, an Alleghenian age of deformation is indicated.

The HVB has been the site of detailed mapping and structural analysis which have defined the deformation processes in the belt (Marshak 1986a; 1986b) and the development of microstructural features (Marshak and Engelder 1984). The geochemistry of cleaved and uncleaved limestone, and related veins in the HVB was addressed by Bhagat and Marshak (1990). More recently Schimmrich and Marshak (1998) presented an abstract of studies concerning mineral geochemistry and fluid inclusion data on HVB veins. They suggested spatial variation in fluid temperatures during vein formation, and called for relatively high water-rock ratios and involvement of a regional fluid that had interacted with basement rocks. Evans and Battles (1999) have provided a well-constrained model for regional fluid migration and vein formation in the Valley and Ridge Province. Their study provides a useful comparative framework for the research reported in this paper.

Helderberg Group and Onondaga Formation carbonate rocks in the HVB near Catskill, New York (Fig. 1) host numerous syntectonic calcite (+/- quartz) veins. Fibrous veins are developed on bedding-plane slip surfaces; veins hosting coarsely crystalline blocky calcite and quartz are widely distributed within coherent limestone beds that lie between bedding plane faults. Calcite veins that apparently post-date deformation are also present. In this paper we present fluid inclusion and stable isotope data that help to constrain the composition of mineralizing fluids, the temperatures and pressures of vein formation, and the conditions of structural deformation within the HVB.

Sampling Localities

Samples of coarsely crystalline calcite and quartz showing well-developed crystal terminations were gathered at three localities in the HVB near Catskill, New York (Fig. 1c). Samples selected showed clear linkages to HVB deformational structures but contained no macroscopic evidence deformation of the crystalline mineral. Co-existing quartz and calcite were selected to allow for oxygen isotope geothermometry, and crystalline quartz was preferred for fluid inclusion...
microthermometric studies because of its relative resistance to stretching during heating of prepared samples.

Site RT23AW is located on NYS Route 23A immediately west of the I87 underpass (near optional Stop B in the guidebook of Marshak 1986b) in an asymmetric anticline developed within coarse bioclastic, cherty limestone of the Onondaga Formation. The material sampled at site RT23AW is from a vuggy area within an otherwise fibrous calcite vein developed on a bedding plane fault.

Site RT23AE (Stop 4 of Marshak 1986b) samples were taken from quartz-calcite veins developed as extensional features in beds of irregularly folded Glenerie Formation of the Helderberg Group. Small folds at this site are related to a detachment fault between the Glenerie and overlying siltstones of the Esopus
Formation, which possess a strong metamorphic cleavage at this locality.

A quartz-calcite vein hosted by the New Scotland Formation was sampled at Site CC RT23 (Stop 2A of Marshak 1986b). This vein developed as a tapering extension fracture within a limestone bed adjacent to a bedding plane fault. Samples of calcite from a late, post-deformational planar fracture fill vein (CCRT23-V) were also collected at this locality.

Sample Preparation and Analytical Methods

Isotope analyses: Immediately adjacent well-terminated quartz and calcite crystals were removed from hand samples. Two samples of quartz-calcite crystal pairs were selected from each sampling site. 2-5 mm of the tip of each crystal was crushed and powdered for isotopic analysis. Calcite samples were analyzed for carbon and oxygen stable isotopes at SUNY Albany’s Stable Isotope Ratio Mass Spectrometer (SIRMS) Laboratory in the Department of Earth and Atmospheric Sciences. Samples of powdered calcite were placed in small septum-capped glass chromatography V-vials and loaded into a heated rack controlled at 0.1°C. A needle sequentially punctures each vial’s septum, injecting 100% phosphoric acid into the sample vial. The carbon dioxide that is evolved during acid digestion of the calcite is passed to a Micromass Optima gas-source triple-collector mass spectrometer for isotope ratio determination. Replicate sample analyses indicate that carbon and oxygen SIRA were performed at a precision of +/- 0.01 per mil.

Quartz samples were analyzed for oxygen SIRA at Krueger Geochron Labs using standard techniques. Replicate sample analyses indicate oxygen SIRA of quartz were performed at a precision of +/- 0.1 per mil.

Fluid Inclusion Analyses

Quartz crystals selected for stable isotope analysis (tips removed) were used for preparation of doubly polished chips for fluid inclusion analysis. Chips were prepared by sawing the crystal perpendicular to the c-axis and hand-polishing the cut face with the cut crystal held in dental wax. The polished face was then mounted with ‘superglue’ onto standard thin-section plates, cut off and coarse ground on a single-arm Microtec thin-section machine. The second side of the chips were then fine-polished and removed from the plates by dissolving the superglue in acetone. Care was taken to not heat the chips above 50°C during the preparation process. In general, the prepared quartz chips were 4-10 mm in diameter, 0.3-1.0 mm in thickness and retained the original crystal face boundaries (Fig. 2A). Calcite cleavage fragments of suitable size were also selected for fluid inclusion examination.

Fluid inclusion microthermometric studies were done using a Fluid, Inc. USGS-design heating-cooling stage. The thermocouple was calibrated at 0°C using an ice-water bath, and at 374.1°C (water critical point) and -56.6°C (CO₂ triple point). Heating runs on individual samples were performed prior to freezing runs to minimize the possibility of inclusion stretching by freezing of ice (Lawler and Crawford 1983). All quantitative measurements were taken on single fluid inclusion assemblages (FIA) that could be monitored within a single field of view so that sudden changes in liquid-vapor ratios could be observed. All quantitative analyses reported were taken from quartz. Well-formed, regular fluid inclusions were selected for analyses. Data was recorded only for inclusions for which phase changes could be reproduced within +/- 1°C, and in most cases phase changes were reproducible within +/- 0.2°C. Fluid inclusion properties were also studied by crushing small (0.5-2 mm. gross diameter) crystal and cleavage fragments in kerosene using the techniques described by Roeld (1986).

RESULTS

Stable Isotopes.-- The results of stable isotope analyses of quartz and calcite are presented in Table 1. δ¹⁸O values are given in reference to the SMOW and PDB standards; δ¹³C is reported relative to PDB. Table 1 includes analyses of one sample of Gleanerie Limestone (RT23AE - LS) and Onondaga Formation chert (RT23AQ - CHT). Data from Bhagat and Marshak (1990) are included for reference. Also shown in Table 1 are equilibrium temperatures of precipitation based on the quartz-calcite stable isotope geothermometer of Sharp and Kirschner (1993). Temperature ranges were calculated using 0.1 +/- range for δ¹⁸O in quartz, which was the maximum replicate error within all isotopic analyses.

The range of quartz-calcite isotopic temperatures (maximum of 315°C; minimum 219°C; mean 254°C) is larger than the range of fluid inclusion homogenization temperatures observed (see below), although the mean temperature is in general agreement with fluid inclusion data. The wide range of isotopic temperatures may reflect the rather coarse level of sampling, since the crystal tips selected may not have grown at the same time.

Stable isotope signatures of four calcite samples from the late vein at site RT23CC are rather different from all other samples analyzed. The lighter δ¹⁸O values suggest precipitation from isotopically distinct waters or at significantly higher temperatures. The lack of quartz in this vein precluded calculation of stable isotope equilibrium temperatures. Fluid inclusion data from calcite in this vein is reported below.

Fluid Inclusions

Quartz crystal sections contain clearly defined growth zones marked by abundant fluid inclusions. These inclusions are apparently primary, and are of two types; 2-phase aqueous inclusions (LVA) and inclusions that contain water and methane (plus minor carbon dioxide and/or higher hydrocarbons-LVAO). LVA and LVAO inclusions form discrete bands
Figure 2. A, B. Section of quartz crystal cut perpendicular to C-axis showing crystal margin and bands of primary inclusions parallel to growth face. Bands of inclusion are graphically enhanced in B. Width of field in A and B is approximately 6 mm. C, D. Typical LVA (2-phase water) inclusions. Scale bar for each is 25 μm. E, F. Typical LVAO (water plus methane) inclusions. Scale bar for each is 20 μm. G. Type VO (methane plus minor carbon dioxide) inclusion. Scale bar is 40 μm. H. Assemblage of type VO inclusions in secondary fracture in quartz. Scale bar is 125 μm.
Table 1. Stable Isotope Data.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Mineral</th>
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<th>δ^13C PDB</th>
<th>Notes</th>
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<td>CC-RT-23-1</td>
<td>Calcite</td>
<td>21.50</td>
<td>-9.08</td>
<td>Syntectonic vein</td>
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<td>-9.09</td>
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<td>--</td>
<td>Syntectonic vein</td>
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<tr>
<td>CC-RT-23-4</td>
<td>Quartz</td>
<td>24.55</td>
<td>--</td>
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</tr>
<tr>
<td>RT-23AW-1</td>
<td>Calcite</td>
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<td>-8.90</td>
<td>Syntectonic vein</td>
</tr>
<tr>
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<td>-8.94</td>
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<td>--</td>
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</tr>
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<td>24.1</td>
<td>--</td>
<td>Syntectonic vein</td>
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<tr>
<td>RT-23AW-CHT</td>
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<td>+0.60</td>
<td>Chert nodule in Edgecliff member, Onondaga Formation</td>
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<tr>
<td>RT-23AW-LST</td>
<td>Calcite</td>
<td>22.52</td>
<td>+0.60</td>
<td>Bulk uncleaved limestone, Glenerie Formation</td>
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<td>RT-23W-V1</td>
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<td>-12.20</td>
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</tr>
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<td>-12.11</td>
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</table>

Mean of 10 strongly cleaved limestones*
Mean of 11 weakly cleaved limestones*
Mean of 11 uncleaned limestones*

Sample Pairs for Quartz-Calcite Thermometry

<table>
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<th>Calculated Temperature**</th>
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<td>CC-RT-23-1,3</td>
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<tr>
<td>CC-RT-23-2,4</td>
<td>243°C</td>
</tr>
<tr>
<td>RT-23AW-1,3</td>
<td>226°C</td>
</tr>
<tr>
<td>RT-23AW-2,4</td>
<td>219°C</td>
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<tr>
<td>RT-23AW-1,3</td>
<td>310°C</td>
</tr>
<tr>
<td>RT-23AE-2,4</td>
<td>281°C</td>
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</tbody>
</table>

* Data from Bhagat and Marshak (1996)
** Quartz-Calcite equilibrium temperatures calculated using constants of Sharp and Kirschner (1969)

of one type that are bounded by growth zones (Figs. 2a, 2b). Both inclusion types are regular to elongate in form (Figs. 4c, 4e). Inclusions used in microthermometric study were 10 to 40 microns in length, and regular in form. When LVAI inclusions are crushed in kerosene, the vapor bubble simply collapses, suggesting rapid contraction of the fluid. LVAI inclusions emit a trail of bubbles that dissolve in kerosene, suggesting the vapor phase expands and consists of methane. Some LVAI inclusions emit bubbles that do not completely dissolve in kerosene, suggesting that some carbon dioxide may be present (Roedder 1986). Given the small size of inclusions and the rapidity of gas escape and dissolution of methane, the relative proportions of water, methane and carbon dioxide cannot be reliably estimated. That bubbles of methane are clearly observed suggests at least a few thousand (1,000-10,000 ?) ppm methane are present in the LVAI inclusions.

Quartz crystals also contain abundant secondary inclusions that formed along fractures that cross-cut growth bands and terminate at the crystal boundary. These inclusions include 2-phase aqueous inclusions that resemble the LVAI type noted above, and are often associated with gas-rich inclusions (VO) that consist largely of methane and minor carbon dioxide (Fig. 4g). Type VO inclusions emit a stream of vapor bubbles that dissolve in kerosene when crushed (methane or other hydrocarbon gas), plus a minor complement of bubbles that do not dissolve (carbon dioxide?). The healed fractures that host type VO inclusions also contain films of dark brown material (bitumen; anthraxolite?).

Post-tectonic vein calcite samples from CCRT23 contain type LVAI inclusions and type VO inclusions. Inclusions in this calcite generally lie along planes parallel to cleavage, and are assumed to be secondary in origin.

Microthermometric analyses: The results of microthermometric study are presented in Table 2. Type LVAI and LVAO inclusions were heated using the ‘cycling’ technique (Goldstein and Reynolds 1994) to determine homogenization temperatures (T_h, T_m) within +/- 0.2°C, based upon replicate analysis of single inclusions. Within the same sample and in adjacent growth bands, type LVAO inclusions generally exhibit slightly higher homogenization temperatures than type LVAI. This is consistent with the presence of methane gas within the vapor phase of LVAO inclusions. T_m, for type LVAO inclusions must closely approach the true trapping temperature (T) of these inclusions (Goldstein and Reynolds 1994).

Contents of both LVA and LVAO inclusions form a glassy
yellowish ice upon cooling below -40°C. The vapor bubble in each type is compacted and distorted by ice formation, precluding lower-temperature study of the vapor phases in these inclusions. The ice typically begins to melt at -22 to -18°C, and in type LVA inclusions, melting of water ice is complete in the range of -3.1 to -1.1°C (Table 2, Fig. 3a). Hydrohalite was observed only near the eutectic point during freezing-melting runs, consistent with relatively low salinity of the waters in the inclusions (Goldstein and Reynolds 1994).

In type LVAO inclusions, the final melt of water ice was very difficult to observe, since these inclusions commonly formed a yellow-brown isotropic solid intermingled with water ice crystals. This yellow-brown solid adhered to the margin of the vapor bubble during water ice melting, and persisted on warming of the inclusion above 0°C. This behavior is consistent with the presence of methane-water clathrate. In some cases, the solid persisted to near room temperatures (~23°C), suggesting that some higher molecular weight hydrocarbons were present in these inclusions. Because of this effect precise determination of final clathrate melting temperatures was not possible. Upon warming, VO inclusions homogenize in the range -82.7 to -86.7°C, indicating that these inclusions consist almost entirely of methane.

LVA inclusions in calcite from sample CCRT23-V were also examined using microthermometry. These inclusions homogenize on heating at temperatures of ~137 to 150°C, and form water ice which melts at ~3.4 to -0.4°C. These data are reported recognizing the potential unreliability of fluid inclusion microthermometric data from calcite, and the apparently secondary origin of these inclusions. The

Figure 3. A. Plot of final ice melt temperature vs. homogenization temperature for type LVA (2-phase water) inclusions from all sample sites. B. Histogram of all homogenization temperature data.

Figure 4. Plot illustrating the range of oxygen isotope composition of water in equilibrium with host limestone (dotted line) and chert (solid line). Black square shows likely range based on fluid inclusion temperature data.
relative low homogenization temperatures suggest that the relatively lighter \( ^{18}O \) values for this calcite are due to precipitation from isotopically lighter waters rather than precipitation of calcite at higher temperatures than syntectonic vein calcite.

**DISCUSSION**

**Fluid Inclusions**

Fluid inclusion homogenization temperatures from type LVAO inclusions are likely very near the true trapping temperatures of inclusion formation and quartz crystal precipitation. The presence of free methane in an aqueous inclusion assures that the contents are held near the trapping pressure (Reynolds and Goldstein 1994), and thus the pressure correction required is negligible. Except for one FIA in the outermost inclusion band from one crystal at site RT23AW, the \( T_{ho} \) values range from 236 to 291°C, suggesting that the majority of syntectonic vein mineralization took place within this temperature range. \( T_{ho} \) for aqueous inclusions in quartz are generally slightly lower than \( T_{ho} \) in the same sample. The quartz-calcite oxygen isotope temperatures (Table 1) also fall within the general range of fluid inclusion temperatures, but these values may be
less reliable because of the coarseness of sampling. However, the reasonable agreement of these two separate approaches to geothermometry suggests that the values are meaningful. The temperatures determined here are somewhat higher than the ranges reported by Schimminich and Marshak (1998) who suggested that vein forming fluids were in the range of 180-250°C, with higher temperatures occurring in the northern part of the Hudson Valley Belt near Albany, NY.

Isotopic Signatures and Salinity of Precipitating Waters

Fluid inclusion homogenization temperature may be used to calculate the isotopic signatures of a range of waters in equilibrium with quartz and calcite in the veins analyzed. The constants of O’Neil, et al (1969) for calcite and Clayton, et al (1972) for quartz, the isotopic data of vein quartz and calcite, plus host limestone values from this study and Bhagat and Marshak (1994) and one chert analysis allow calculation of isotopic values of equilibrium waters as shown in Table 3. Figure 4 illustrates the range of calculated δ¹⁸O in equilibrium with host limestone and chert as a function of temperature.

The range of δ¹⁸O of the waters from which syntectonic vein minerals precipitated (+14.7 to +16.1 per mil SMOW) is similar to the values of δ¹⁸O for waters in equilibrium with host limestone and chert within the temperature range determined from fluid inclusions. This suggests that fluid involved in syntectonic vein formation could have been derived internally from connate formation waters within the local Devonian sequence and that the δ¹⁸O of vein-mineralizing waters was buffered by host carbonate and chert. These water isotopic values suggest that significant isotopic exchange between connate water and host rocks occurred during the evolution of the fluid. Waters of this sort are classified as ‘evolved’ (Shepard 1986) due to their isotopic signature. Higher salinities than those observed in the fluid inclusion analyses in the HVB samples (range 2.5-3.2 % NaCl equivalent based on final melting temperatures of water ice) are common in evolved sedimentary brines. This indicates that waters in the HVB did not interact with evaporite salts, which would raise the salinity significantly. The composition of the fluids, based on Tm ice, is essentially the same as seawater (Tm = -1.9°C). It may be that the low salinities observed in the Catskill-area HVB vein systems are due to the presence of a significant volume of water derived from dehydration of hydrous minerals within the clastic units of the local stratigraphic section. For example, water derived from clay during re-crystallization of smectite and vermiculite to illite, and other mineral transformations related to compaction and metamorphic cleavage formation may dilute connate formation waters because only limited amounts of new solute are added to the fluid system (Mullis, et al 1994). Dewatering of terrigenous clastic sediments would also provide a source of radiogenic strontium, consistent with the Sr-isotope data of Schimminich and Marshak (1998).

Water in equilibrium with calcite in the post-tectonic vein at CCRT23 is significantly lighter (δ¹⁸O = +4.9 to +6.2 per mil SMOW) than the calculated waters from syntectonic veins and host rock equilibria. The temperatures selected for calculation of isotopic equilibria at CCRT23-V are based on inclusions in calcite which may well be secondary in origin and record a later, lower temperature event. Using a temperature of 250°C to calculate equilibrium waters, the isotopic values for the post-tectonic vein waters are in the range δ¹⁸O = +11.5 to +12.6 per mil SMOW, or slightly lighter than the syntectonic vein waters. If the post-tectonic vein calcite is a lower-temperature phenomenon, then the lighter isotopes may reflect

Table 3. Isotopic Composition of Waters Based on Equilibrium Calculation.

<table>
<thead>
<tr>
<th>Sample/Site</th>
<th>Mineral</th>
<th>δ¹⁸O Mineral</th>
<th>Fluid Temperature*</th>
<th>δ¹⁸O Water*</th>
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<td>CC-RT23</td>
<td>Calcite</td>
<td>21.5</td>
<td>263</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>24.5</td>
<td>263</td>
<td>16.1</td>
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<td>14.7</td>
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<td>RT-23AW LST</td>
<td>Calcite</td>
<td>22.5</td>
<td>250</td>
<td>15.7</td>
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</table>

* Average of LVAO Tn at sample site
** Calculated using constants of O’Neil, et al. (1969) for calcite and Clayton, et al. (1972) for quartz
infiltration of meteoric waters during later stages in the evolution of the HVB.

**Pressures During Vein Formation**

The $T_{h}$ of LVAO inclusions record temperatures very near the true trapping temperatures but since the relative proportions of the water and methane (plus minor carbon dioxide and possibly higher hydrocarbons) were not determined, reliable isochors cannot be calculated for these inclusions. Shown in figure 5 are thermobaric gradients of 25 and 40°C km$^{-1}$ for both lithostatic and hydrostatic systems. The lower gradients are consistent with values for the modern Appalachian Plateau (Natheson and Guffanti 1988) and for the modern Alpine foreland. (Rybach and Bodmer 1980). The band of temperatures shown (244-263°C), represents the likely range of syntectonic vein mineralization based upon the average Thao from the three localities. The intersection of this temperature band with the LVA isochores (calculated using the method of Brown and Lamb 1989) provides a range of trapping pressures for the LVA inclusions. The pressures determined by this method are in the range of 320 to 480 b, which corresponds to a burial depth of 3.2 to 4.8 km if the pressures were hydrostatic or 1.4 to 2.1 km if the pressures were due to the lithostatic load. Note from figure 5 that these pressures require a relatively high geothermal gradient at the time of HVB syntectonic vein mineralization. A gradient of 40°C or more per kilometer, which is consistent with these data, suggest that the rocks and water in the HVB may have been heated by an external source. The deep burial depths suggested for the Paleozoic strata in New York State by other workers (e.g. Friedman 1987a, 1987b; Friedman and Sanders 1982; Golam and Friedman 1995) are not necessarily challenged by these results. Hot fluids from more deeply buried portions of the basin may have traveled up-dip during maximum loading of the basin and carried heat into the HVB. This mechanism has been invoked to explain anomalously high vitrinite reflectance values in upper Paleozoic rocks of the Appalachian Plateau (Zhang and Davis 1993). The fractured rocks within the decollement zone represented by the HVB may extend into the subsurface to the south and west and provide a high-permeability conduit for deep hot fluids. Deep basinal fluids identified in other Appalachian foreland vein mineral systems are usually of much higher salinity than those observed in the HVB (e.g. Evans and Battles 1999). Alternatively, late Devonian and Carboniferous granitic plutons related to those emplaced in eastern Connecticut and Massachusetts may be present at depth beneath the HVB, and promoted the convective circulation of locally derived connate geothermal waters.

Figure 5 also presents the 'bubble point curves' (P, T of equilibrium solubility of methane in water) for 5000 ppm methane in 0.0 and 1.0 molar NaCl equivalent waters. Final-ice melt temperatures indicate a NaCl-equivalent molality of ~0.5 in LVA inclusions. Type LVAO inclusions contain methane, plus variable but minor amounts of carbon dioxide. The 5000 ppm bubble point curves are therefore shown for reference only, but indicate that the temperatures and pressures inferred from other considerations are consistent with methane.

**Figure 5. Summary plot showing fluid isochors, methane bubble point curves, fluid inclusion homogenization temperatures and range of geotherms. See text for full discussion.**
solubility relationships. In the P, T range of 320-480 bars, 246-263°C, a few thousand ppm methane could be in solution with waters of the salinities determined, and trapped as type LVAO inclusions.

In the quartz crystals examined, type LVA and LVAO inclusions occur in discrete, alternating growth-zone bands (Fig. 2b). This alternation suggests that low-methane and high-methane waters were available at different times during vein mineral crystallization. This may have been controlled by the dynamics of methane generation or by variations in pressure at the time of trapping of an inclusion band. In a dynamic deformational zone like the HVB, pressures within vein fluid may have risen to lithostatic load at times, and then dropped to hear hydrostatic. Lower pressure conditions would favor the formation of methane-poor inclusions, since solubility of the gas would be reduced if temperature were held constant.

**Burial Depth**

The coarse, blocky vein mineralization in the HVB and the presence of open vugs with well-terminated crystals within near-horizontal syntectonic veins suggest that hydrostatic pressures were at least at times sufficient to hold open fluid-filled space against the ambient lithostatic load (Marshak 1986b). This suggests that the system was in a state of fluid overpressure at times, or that the depth was shallow enough such that the lithostatic load was balanced by a normal hydrostatic gradient. As noted above, burial depths in the range 1.4-2.1 km are indicated if lithostatic loading is assumed, whereas depths of 3.2-4.8 km are indicated if purely hydrostatic pressure is assumed.

**Carbon Isotope Signatures and Organic Maturation**

Carbon isotope signatures of the vein calcite in the HVB were controlled by the source of carbonate in the precipitating fluid. Antony, as shown above, the fluids were generally in oxygen isotopic equilibrium with the host carbonate rocks and chert, and the carbon isotope signatures of vein minerals are broadly similar to the host limestones. Generation of carbon dioxide from maturing organic matter during heating and burial may also affect the carbon isotope system. In general, carbonate derived from decarboxylation will be somewhat lighter in terms of carbon isotopes than limestone-derived carbonate. The range of carbon isotopes in the syntectonic vein carbonate apparently reflects mixing of limestone-buffered (heavier) carbonate with lighter organic derived-carbonate and is similar to that observed in other syntectonic vein systems (Dietrich, et al 1983). The post-tectonic vein at CCRT23 carries significantly lighter carbon than all other samples, suggesting proportionally greater involvement of organic-derived carbonate.

The presence of methane-bearing inclusions in conjunction with heavy ‘dead oil’ residues in healed fractures within HVB vein minerals indicates that petroleum maturation must have occurred prior to or during HVB deformation. The temperatures determined from fluid inclusion microthermometry and stable isotope equilibria are above the normal range for generation of crude petroleum, consistent with petrographic observations and regional petroleum occurrence.

**SUMMARY**

Stable isotope analysis of co-existing quartz and calcite in syntectonic veins from the HVB near Catskill, New York indicate mineral precipitation at temperatures between 219-315°C.

Primary fluid inclusions in syntectonic quartz that contain water and methane have homogenization temperatures of 236-291°C. These homogenization temperatures are near the true trapping temperatures, and further constrain the temperature of quartz precipitation.

Final ice melt temperatures in primary aqueous inclusions in quartz indicate salinities near seawater composition for vein mineralizing fluids.

Pressures determined from methane-water equilibria and aqueous inclusion isochore intersection suggest burial depths in the range of 1.4-4.8 km during syntectonic vein formation. The relatively high local geothermal gradients required to generate the temperatures observed at these depths suggest transport of fluid from deeper within the orogen, perhaps facilitated by enhanced hydraulic conductivity in the HVB decollement zone. The relatively shallow burial depth during vein formation does not preclude either Acadian (Late Devonian) or Alleghenian (Pennsylvanian-Permian) tectonism in the HVB. The relatively high temperatures require either a deeply buried basinal source of fluids to the west (more consistent with a late Paleozoic, Alleghenian timing) or a nearby source of magmatically heated water (more consistent with the late Devonian, Acadian-age intrusion of granites in western Connecticut).

Calculation of isotopic equilibria among host limestone, chert and vein minerals at the temperatures indicated by fluid inclusions indicate that vein-mineralizing fluids were buffered by host rock chert and limestone. Internal derivation of mineralizing fluids is consistent with the near-seawater salinity of fluid inclusions.

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